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Use of Char for Management of Paint Processing Waste

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Use of Char for Management of Paint Processing Waste

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ABSTRACT

Volatile organic compounds (VOCs) and paint sludge are generated by painting operations at automobile assembly plants. This study's goal was to demonstrate that paint sludge can be converted to adsorbents for the capture of VOCs. Combining coal with paint sludge was projected to improve the adsorbent quality and might improve economics show a significant "economy of the scale of operation". The Illinois State Geological Survey (ISGS) made a series of activated carbons from 1) dried paints, 2) overspray paint materials captured at an assembly plant, 3) coal and 4) with mixtures of paint products with coal. Adsorption capacities of the ISGS carbons were determined in the Ford Research Laboratory with p-nitrophenol as a model adsorbate.

Char making, or carbonization as it is often called, is the very old process of heating an organic substance in the absence of air to drive off the noncarbon components, primarily compounds of oxygen and hydrogen. Carbohydrates (a shortened version of carbon hydrates) derive their name from the early observation that they leave carbon when dehydrated by heating in the absence of air or by chemical agents such as sulfuric acid. Organic substances that do not melt, such as wood or nut hulls, produce a porous charcoal of the type marketed for use in home cooking grills. Removing carbon from a char by gasification enlarges the pore sizes and alters the pore size distribution resulting in activated carbons that have high internal surface areas. These activated carbons or those produced by chemical activation are the materials used in adsorption processes.

Initial charring of dry paint demonstrated that the product was not a carbon with appreciable surface area. Additionally the paint material went through a melting stage during charring. ISGS researchers turned then to chemical activation with potassium hydroxide (KOH) as a means of making an activated product. Properties of the control char derived from Illinois coal approximated those of Calgon Corporation commercial carbons. Carbon black and titanium dioxide (TiO_2) are pigments in automotive black and white paints, respectively. White paints generally have much higher ash contents than black paints. The ash content of black paints from the two manufacturers in this study were quite different suggesting some noncarbon black pigment was used. The lower the ash content of the adsorbents made, i.e. the more carbon, the better were the adsorbent properties. There was no evidence that ash-forming materials assisted in pore development. The quality of sludge-derived adsorbent was between those of adsorbents derived from black and white paints. Blending coal with white paint improved the adsorption capacity of adsorbent.

The results of the tests completed on the adsorbents made in this study warrant further study, both technical and economic. Tests using p-nitrophenol to compare adsorption properties of paint-derived adsorbents with those of commercially available adsorbents are being extended at Ford to include selected paint solvents. Confirmation at this level may justify larger scale production of the adsorbents for testing at a scale that provides information useful for preliminary economic calculations.

EXECUTIVE SUMMARY

Automotive painting operations generate a variety of wastes, primarily volatile organic compounds and paint sludge. The objectives of this study were: 1) to produce carbon-based adsorbent materials from dried paint materials and 2) to compare the adsorption capacities of the adsorbents produced from paint and paint sludges, or from mixtures of paint with coal, to those of commercially available adsorbent. Chars were chemically activated during pyrolysis by using potassium hydroxide (KOH).

The technical feasibility of producing activated carbon (AC) from real and simulated paint sludge was examined jointly by the Ford Research Laboratory (FRL) and the Illinois State Geological Survey (ISGS). The ISGS produced nine powdered activated chars (carbons) using several dried paints, a paint sludge, a coal, and a mixture of coal and dried paint. A pelletization step will likely be required to convert the powder to granular activated carbon (GAC), the physical form used in most systems adsorbing VOCs from gaseous streams. FRL conducted liquid-phase adsorption experiments using p-nitrophenol as the adsorbate to evaluate adsorption capacities of the chars and to compare the results with those obtained using commercially available activated carbons.

The primary findings were:

- Nonactivated paint chars had very little surface area and no appreciable capacity to adsorb p-nitrophenol. Activated carbons were produced from paint products by first charring a 50:50 weight mixture of KOH and paint product, and then washing away the potassium hydroxide and other components solubilized by the strong base.

- Activated black-paint chars showed substantially larger surface area than white-paint chars, probably due to the white pigment, titanium dioxide, which is not expected to form a porous adsorbent material. Two black-paint chars, WBBP-B and SBBP-A, showed a surface area close to that of an activated char made from a bituminous coal in the Illinois Basin Coal Sample Program (IBC-109) using the same conditions as used for the black-paint chars.

- Activated black-paint chars, produced from manufacturer B's paints, showed unexpectedly high ash contents (21% for WBBP-B and 59.3% for SBBP-B) for a paint using carbon black as pigment.

- The ash content of the white-paint chars was very high (over 80%), as expected because of the white pigment, titanium dioxide.

- The adsorption capacities of the Calgon carbons (BL and F-400) and the IBC-109 carbon were comparable to each other and higher than those of the paint chars.

- The adsorption capacities of the black-paint chars were higher than those of the white-paint chars indicating that the pigment, titanium dioxide, did not participate appreciably in the adsorption of p-nitrophenol or in making the carbon portion or the structure more active.

- The paint-sludge char showed an adsorption capacity and an ash content between those of the black-paint chars and the white-paint chars, as expected for a sludge formed from a variety of paints. The adsorption capacity of the paint-sludge char was found to be a little less than 20% (total weight based) and 50% (ash-free weight based) of the Calgon BL's.

- The fact that coal-paint mix char showed adsorption capacities that are expected for the fraction of coal in the mix suggests that there is no synergism between the white paint's titanium dioxide and coal for producing additional surface area or adsorption capacity. However, it was found that coal could be added to paint sludge to improve the quality of the resulting char and to reduce ash content.

- The slopes of the paint-char adsorption isotherms were close to those of the Calgon carbons and were relatively flat (i.e., n is much greater than 1), indicating that the adsorption capacity of a paint-sludge char could be efficiently used even at relatively low concentrations of a compound such as p-nitrophenol.

- The adsorption capacity at 100 mg/L of p-nitrophenol was found to increase linearly with surface area.

- Chemical activation parameters were not optimized. A KOH/paint ratio other than 1/1 or the use of other chemical agents may improve adsorption properties of chars derived from paint materials.

1.0 INTRODUCTION

During automotive spray-painting operations, the spray-booth air goes through a water scrubber to capture overspray paint particulates. Since the scrubber was not designed for the purpose of removing volatile organic compounds (VOCs) from the booth air, a significant portions of the paint solvents escape the scrubber. Therefore, the spray-painting operations generate wastes in gaseous, liquid, and solid phases: 1) VOCs emitted in stack air; 2) spent spray-booth scrubber water that contains some dissolved VOCs; and 3) paint sludge that results from the accumulation of the captured paint particulates. Currently at automotive assembly plants, gaseous emissions in the booth air of automatic spraying sections are controlled by using a vapor-phase activated carbon adsorption/incineration system to remove VOCs. The spent scrubber water is periodically discharged to a municipal wastewater treatment plant. The paint sludge is landfilled. The study reported herein addresses the solid wastes (paint sludge) as part of an effort to explore the possibility of recycling a processed paint sludge that by converting it to an adsorbent for the VOCs. There are several types of commercially available vapor phase adsorption systems. The one being used at Ford plants is based on a rotary adsorber that contains activated carbon fiber. This adsorber goes through continuous adsorption/desorption cycles as it rotates. This system is just one of many vapor phase adsorption systems. Identifying precisely the fate of the spent coal/paint char, i.e, whether it would be discarded or regenerated, was beyond the objectives of this preliminary study. While recovery of the VOCs for reuse appears to be an attractive possibility, the technical feasibility must be determined. Chemical interaction of different VOCs of various types make it less likely that recovery will be feasible. There have already been unsuccessful attempts to recover VOCs from some of the vapor phase adsorption systems.

One of the major factors that affects the costs of handling and disposing of paint sludge is the volume of the sludge. In order to reduce sludge volume, some automotive assembly plants have been drying the sludge. This reduces transportation and disposal costs and might make it possible to reuse the dried sludge for filler or to make low-quality paints (Berghoff, 1993).

Another process that could be used to reduce sludge volume is pyrolysis. The pyrolysis of paint sludge not only results in a smaller volume than that achieved by drying, but under some conditions could produce an activated char that could be used as an adsorbent. This pyrolysis and the subsequent use of the resulting char in a spray-booth scrubber would have dual benefits. First, the volume reduction is expected to be much more than that by drying alone because the pyrolysis of paint sludge not only removes moisture but also breaks down organic matter. Secondly, the pyrolysis of paint sludge coupled with an activation step can produce activated carbon, which can be put back into the scrubber water as an adsorbent to remove VOCs (especially nonpolar VOCs) from the booth exhaust air. Kim and Pingel (1989)

experimentally and mathematically showed that toluene was effectively removed from air using a powdered activated carbon/water slurry in a reactor.

In order to examine the technical feasibility of producing activated carbon from paint sludge, a joint research program was developed between Ford Research Laboratory (FRL) (Dearborn, Michigan) and the Illinois State Geological Survey (ISGS) (Champaign, Illinois). In this program, the ISGS was responsible for producing and characterizing chars from paints, paint sludge, and a mixture of paint with coal. FRL was responsible for supplying the paint materials and performing adsorption studies with the chars. The ISGS supplied nine chars derived from six dried paints (simulated paint sludges), a paint sludge, a coal, and a coal/paint mixture. FRL conducted liquid-phase adsorption experiments to evaluate adsorption capacities of the chars and compared the results with those of commercially available activated carbons. The adsorbate selected for this study, p-nitrophenol, has been frequently used as a model adsorbate by many researchers in the environmental field (Snoeyink et al., 1969; Kim et al., 1976; Fritz and Schlunder, 1981; Kim et al., 1990; Kim and Cognata, 1990). The use of this adsorbate facilitates comparisons of the adsorption properties of adsorbents made in this study with those reported in the literature. Although a direct relationship is not expected between the adsorption capacities for p-nitrophenol and paint solvents on two adsorbents, two adsorbents with comparable capacities for p-nitrophenol are likely to exhibit comparable capacities for paint solvents in a general sense.

2.0 MATERIALS AND METHODS

2.1 Materials

The adsorbents used in this study are listed in Table 1. The table includes the base materials used (coal, paint sludge, and paints), the nature of solid materials in paints, and the sources of the paint materials. Calgon F-400 (Calgon Corp., Pittsburgh, Pennsylvania) was not used in this study. However, a set of adsorption data on the F-400 carbon was obtained from the literature (Kim and Cognata, 1990) and was used for data analysis. Calgon BL and F-400 are similar except in particle size (Calgon, 1976; Calgon, undated).

Six paints were obtained from two paint manufacturers: two solvent-borne paints (black and white) from manufacturer A; two solvent-borne paints (black and white) from manufacturer B; and two water- borne paints (black and white) from manufacturer B. According to Material Safety Data Sheets, all paints contained a melamine-formaldehyde resin and other resins. The black paints contained carbon black as a pigment whereas the white paints contained titanium dioxide as a pigment.

The paint sludge was obtained from an assembly plant in a dry form. In that plant, overspray paint materials were captured using a wet scrubber, detackified (made nonsticky) using organic polymers, collected through flotation, and dried using a thermal dryer.

The coal was the Herrin (Illinois No. 6) coal from lot IBC-109 in the Illinois Basin Coal Sample Program. The program is sponsored by the Illinois Department of Energy and Natural Resources through its Coal Development Board and the Illinois Clean Coal Institute. The coal sample bank is located at the ISGS. Lot IBC-109 is a low sulfur Illinois coal. Its total sulfur content of 1.2% is low enough to permit making metallurgical grade coke from this coal. The coal-derived char served as a control with which to compare the properties of chars made from the coal/paint mix, the dried paints, and the paint sludge and also those of commercially available activated carbons.

The coal-paint-mix char was prepared by mixing the Illinois coal (IBC-109) with a solvent-borne white paint (manufacturer B) prior to pyrolysis.

p-Nitrophenol (99+%) was obtained from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. The pKa of p-nitrophenol is 7.15 (Weast and Shelby, 1982). Reagent-grade potassium hydroxide (85.0% minimum assay) was obtained from EM Science, a Division of EM industries, Inc. and an associate of E. Merck, Darmstadt, Germany. The weight ratios used to describe KOH activation were based on the total reagent weight, not the KOH content of the material. Reagent-grade concentrated

Table 1: Adsorbents Used in This Study

Adsorbents		Base Materials	Solids in Paints	Sources
Name	Type			
Calgon BL	PAC[1]	Bituminous Coal	-	Calgon Corp.
Calgon F-400	GAC[2]	Bituminous Coal	-	Calgon Corp.
IBC-109	Coal Char (activated)	Bituminous Herrin (Illinois No. 6) Coal	-	Southern Illinois preparation plant
Coal-Paint Mix	Coal-Paint Mix Char (activated)	A Mixture of Illinois No. 6 Coal and Dried Solvent-borne White Paint	melamine-formaldehyde polymer, polyurethane polymer, titanium dioxide	Southern Illinois preparation plant/ Paint Manufacturer B
Paint Sludge	Paint-Sludge Char (activated)	Dried Paint Sludge	Unknown (a mixture of many paints)	An Automotive Plant
WBBP-B	Black-Paint Char (activated)	Dried Water-borne Black Paint	melamine-formaldehyde polymer, polyurethane polymer, carbon black	Paint Manufacturer B
SBBP-B	Black-Paint Char (activated)	Dried Solvent-borne Black Paint	melamine-formaldehyde polymer, polyurethane polymer, carbon black	Paint Manufacturer B
SBBP-A	Black-Paint Char (activated)	Dried Solvent-borne Black Paint	butylester polymer, melamine-formaldehyde polymer, polyester polymer, carbon black	Paint Manufacturer A
SBBP-A-N	Black-Paint Char (nonactivated)	same as above	same as above	Paint Manufacturer A
3WBWP-B	White-Paint Char (activated)	Dried Water-borne White Paint	melamine-formaldehyde polymer, polyurethane polymer, titanium dioxide	Paint Manufacturer B
SBWP-B	White-Paint Char (activated)	Dried Solvent-borne White Paint	melamine-formaldehyde polymer, polyurethane polymer, titanium dioxide	Paint Manufacturer B
SBWP-A	White-Paint Char	Dried Solvent-borne White Paint	ethylester polymer, melamine-formaldehyde polymer, titanium dioxide, silica	Paint Manufacturer A

[1] Powdered Activated Carbon
[2] Granular Activated Carbon

hydrochloric acid fromFisher Scientific, Fair Lawn, New Jersey, was diluted with deionized water to prepare a 5N solution used to wash the chars. Deionized water was used in all adsorption experiments.

2.2 Analytical Methods

The surface areas of the chars were measured with a Quantachrome Monosorb Surface Area Analyzer produced by the Quantachrome Corporation, Syosset, New York. The Monosorb uses the single point Brunauer, Emmet, and Teller (BET) method for calculating the surface area from the amount of nitrogen adsorbed at −196°C by a sample that has been degassed at 130°C under vacuum prior to introduction of the adsorbate nitrogen.

A Cahn TG-131 thermogravimetric analyzer manufactured by the Cahn Corporation located in Cerritos, California, was used to determine the volatile matter and ash of the samples. The program provided for the determination of weight loss on heating to 950°C at 50°C/min in nitrogen. After holding the devolatilized material at 950°C for 3 minutes, the ash content was determined after cooling down to 750°C and burning the carbon away in air flowing at 100 mL/min.

The concentration of p-nitrophenol was measured using a Lambda 6 UV/visible spectrophotometer (The Perkin-Elmer Corporation of Oakbrook, Illinois) at a wavelength of 317 nm. An ion analyzer Model 960 (Orion Research, Cambridge, Massachusetts) was used to measure pH.

2.3 Experimental Methods

Preparation of Base Materials for Pyrolysis. Each paint was separately dried at FRL by heating it at approximately 50°C in a hood for several weeks until most of the paint solvents evaporated, and then placing it in an oven at approximately 110°C for several days. The paint was further dried at ISGS in a vacuum oven (a Lab-line Duo-Vac oven manufactured by Lab-Line Inst. Inc. in Melrose Park, Illinois) at approximately 100°C under vacuum for approximately two days. Before the vacuum drying, each dried paint was crushed to 16 mesh or smaller, a size suitable for the vacuum drying oven. The "bowl" of the hand-operated crusher was a cup formed by welding a 10 in. (25.4 cm) cylindrical section of 8 in. (20.3 cm) pipe to a heavy-gauge steel plate. The crusher (pestle) was a 25 lb (11.4 kg) disk (1 in. [2.54 cm] thick x 5 in. [12.7 cm] diameter) attached to a T-shaped, 30 in. (76.2 cm) handle suitable for applying pressure and torque from a standing position. Crushing of tarry or spongy paint samples was time-consuming, but it was facilitated by cooling them in liquid nitrogen before crushing. The coal was ground to minus 60 mesh particle size in Model 500 mill manufactured by Holmes Brothers Inc., Danville, Illinois. Neither the coal nor the paint sludge required the vacuum drying.

Pyrolysis. Two pyrolysis methods were used: 1) small-scale charring for initial scoping tests and 2) continuous-feed charring for producing larger amounts of chars. The small-scale charring was carried out under a nitrogen atmosphere (1 liter/minute) in a 1400-W furnace (a Lindberg-type 54232 tube furnace with a Lindberg-type 59344 controller from Lindberg Corporation in Watertown, Wisconsin), which was fitted with a 34 in. (86.4 cm) long by 1.5 in. (3.81 cm) ID mullite tube. A ceramic boat was loaded with a prepared base material, and pushed into the heated zone of the furnace for the desired residence time and then moved to the section of the furnace extending beyond the heated zone to cool. The paints from manufacturer A were pyrolyzed using this method.

The continuous-feed charring was conducted in a continuous-feed charring oven (CFCO), which was patterned after one designed and built at ISGS for thin bed charring of coal (Kruse and Shimp, 1981; Kruse et al., 1988). The char production rate of the CFCO was 100 g per hour. A drawing of the CFCO is shown in Figure 1. A belt of overlapping, stainless steel trays, forming a 5.5 in. (14.0 cm) wide trough, carries the material to be charred through the electrically-heated charring zone. The CFCO can be used at temperatures up to 700°C. The bed depth can be varied from around 1/10 in. (0.25 cm) to 3/4 in. (1.91 cm). The range of residence time is generally from 5 to 45 minutes. The temperature in the oven is regulated by programmable temperature controllers on the heating rods above and below the conveyor belt. The feeder has a slide that is used to regulate the depth of the material on the conveyor. A variable speed motor driving the conveyor regulates residence times in the heated zone. The housing maintains a nitrogen atmosphere in the oven. The nitrogen flows counter to the direction the conveyor belt moves. As the material passes through a heating zone of successively higher temperatures the inert gas removes volatile pyrolysis products to a lower temperature zone insuring that the pyrolysis products do not react with char that has reached a higher temperature. The CFCO was used to produce all activated chars from the coal-paint mix, the paint sludge, and the paints from both manufacturers.

Chemical Activation. Chemical activation was used to increase the surface area of the resulting chars. Except for the coal-paint mix, the base material was mixed with KOH at a weight ratio of 1 to 1 prior to pyrolysis. The weight of KOH was based on the total weight of KOH pellets, not their assayed KOH content. The addition of water and a small amount of detergent facilitated mixing. The detergent used was Alconox made by Alconox, Inc. located in New York City, New York. Most of the added water was removed in the subsequent drying step in which the mixture of KOH and a base material (paint-derived) was occasionally stirred at approximately 100°C for two days under reduced pressure. The dried mixture was pyrolyzed at 600°C for 30 minutes in a nitrogen atmosphere in the CFCO. The pyrolyzed paint/KOH mixture was washed with warm deionized water to remove most of the KOH. It was then soaked in 5N HCl for 15 hours, and washed again with deionized water. The chars were dried at approximately 110°C and stored in a desiccator prior to use.

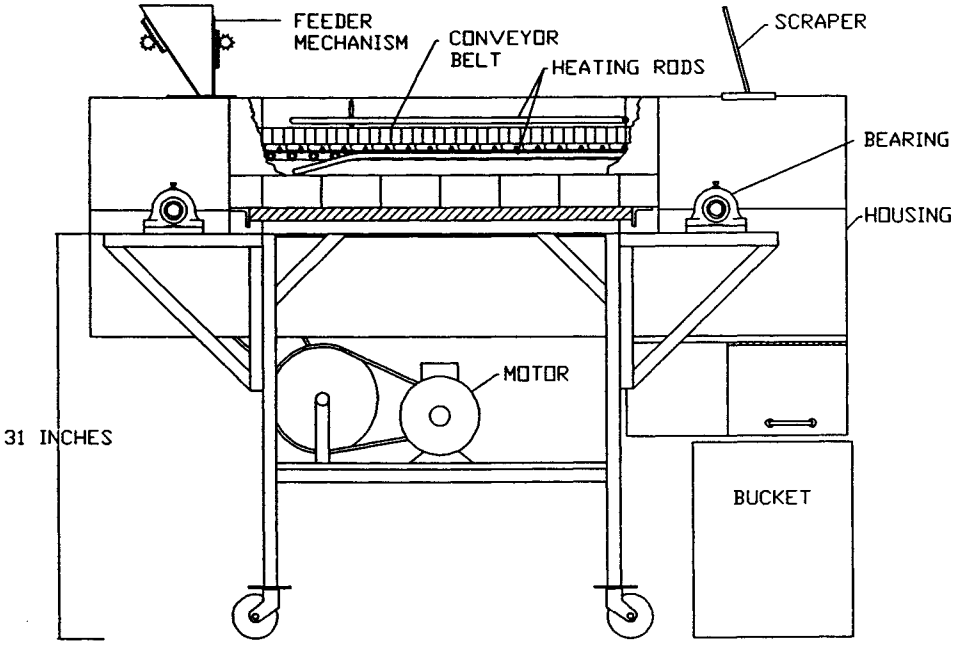

Figure 1: Thin Bed, Continuous-Feed, Charring Oven (CFCO) with Cut Away View of Reactor

The procedure for preparing a coal-paint mix adsorbent involved two mixing steps prior to pyrolysis. A paint/KOH mixture and a coal/KOH mixture were prepared separately and then mixed to yield a coal-to-paint ratio of 9 to 1. The paint/KOH mixture was 1 part solvent-borne white paint (manufacturer B) with 1 part KOH, whereas the coal/KOH mixture was 1 part Illinois coal with 1.5 parts KOH.

Isotherm Experiments. Isotherm experiments were conducted in 250 mL or 125 mL amber glass bottles with Teflon-lined caps. Two or three glass beads approximately 1/8" in diameter were added to each bottle to aid in mixing. Each bottle was prepared by adding predetermined amounts of an adsorbent and filled with a p-nitrophenol solution of a known concentration. Then the bottles were packed into paint cans which were placed on a roller apparatus (Bellco Glass, Vineland, New Jersey) for mixing. After at least four days of mixing for equilibration, the bottles were centrifuged prior to analysis to remove adsorbent particles using a Sorvall RB-5C Superspeed Centrifuge (Du Pont Instruments, Newtown, Connecticut)

All isotherm experiments were conducted at room temperature (21 to 25°C) and at a pH less than 4 to ensure that p-nitrophenol was in the neutral form. A dilute H_2SO_4 solution was used for pH control.

3.0 RESULTS AND DISCUSSION

3.1 Initial Scoping Tests

Initially, the two paints (black and white) from manufacturer A were used to determine whether activation was needed to increase surface area and what type of activation was needed. The selection of these two paints was made based on their pigments (carbon black for the black paint and titanium dioxide for the white paint) to represent two extreme types of paints with regard to their potential ash content after pyrolysis. The moisture-free analyses of the paints confirmed that the white paint had a much higher ash content (24.7%) and a lower fixed carbon content (2.9%) than those of the black paints (0.05% and 4.7%, respectively). With this information, it was concluded that the black paint would result in an adsorbent with a higher surface area than the white paint. Therefore, the pyrolysis of the black paint was conducted with and without activation. The surface areas of both activated and nonactivated char are shown in Table 2 along with those of Calgon BL, Calgon F-400 and an Illinois coal for comparison. The Calgon carbons had higher surface areas than those of the activated paint or coal chars. The nonactivated char had no appreciable surface area.

Table 2: Surface Areas of Activated and Nonactivated Chars and Calgon Carbons

Adsorbents	Surface Area, m^2/g
Calgon BL[1]	1,000-1,100
Calgon F-400[2]	1,050-1,200
SBBP-A-N (Nonactivated Char)	19
SBBP-A (Activated Char)	767
IBC-109 (Activated coal char)	761

[1] Powdered Activated Carbon
[2] Granular Activated Carbon

Adsorption capacities of the chars were also compared with those of Calgon carbons as shown in Figure 2. Because Calgon F-400 has been widely used and tested by many researchers for removing organics from water, it was used as a second reference adsorbent. Only one isotherm point was obtained for the nonactivated char because the amount of p-nitrophenol adsorbed was too small to measure even with high adsorbent dosages of 0.5 g/L to 1.3 g/L. The results of the adsorption experiments clearly showed that 1) the adsorption capacity of the

nonactivated char for p-nitrophenol was insignificant due to the very low surface area; 2) the adsorption capacity of the activated char was comparable to those of commercially available activated carbons; and 3) an activation step was needed if chars from paint materials were to be used as adsorbents.

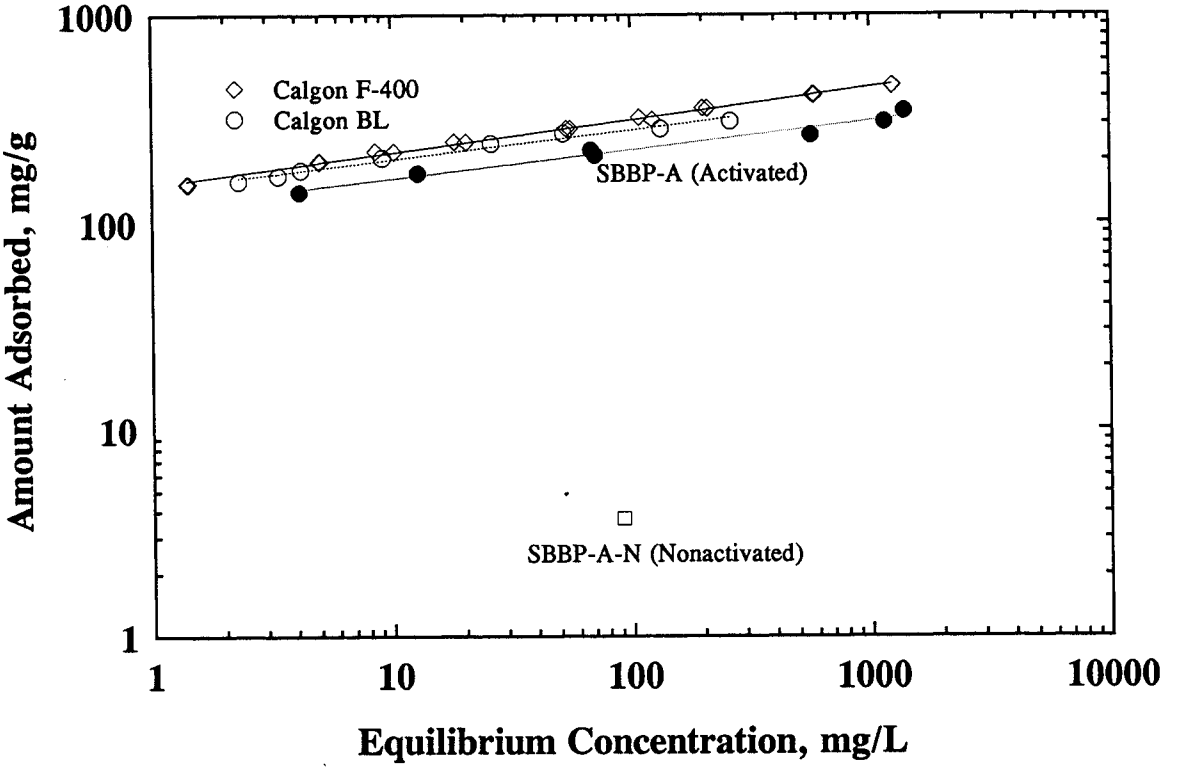

Figure 2: Adsorption of p-Nitrophenol on SBBP-A (Activated), SBBP-A (Nonactivated), and Activated Carbons

Typically, activated carbon is produced from a base material in a fluidized bed through a pyrolysis step under reducing conditions (e.g., under a nitrogen atmosphere) followed by an activation step in the presence of a small amount of oxygen (e.g., 1 % oxygen in high purity nitrogen). In the activation step, some easily oxidizable portions of the charred material are oxidized, resulting in a more porous structure, thus higher surface area. However, this two-step process was found to be inapplicable because initial tests using the small-scale charring oven showed that the paints melted before losing appreciable volatile matter. Therefore, a one-step process, in which pyrolysis

and chemically-aided activation take place simultaneously in a fixed bed, was chosen for this study.

KOH was used for activation in this process. The charred solvent-borne black paint (SBBP-A-N) had a nitrogen surface area of only 19 m^2/g. When ten percent KOH raised the surface area to only 128 m^2/g, the KOH percentage was raised to 50%. Values of 718 and 767 m^2/g were obtained in two tests. The sample with the higher surface area was used for adsorption tests. The process of activation was not optimized. A KOH/paint ratio other than one to one weight ratio or the use of other chemical agents such as phosphoric acid may improve adsorption properties of chars derived from paint materials over those reported (Jagtoyen et al., 1992).

3.2 Physical Characteristics of Activated Chars

The BET nitrogen surface areas of the activated chars were calculated on both a total weight basis and an ash-free weight basis. The results are shown in Table 3 along with the Calgon carbons. The Calgon carbons had higher surface areas than those of the chars prepared for this study including the two in which the Illinois coal was used (IBC-109 and coal-paint mix). The black-paint chars had substantially higher surface areas than the white-paint chars. This was expected because the main pigment used in the white paints is titanium dioxide. Titanium dioxide was not expected to form a porous material although there was the possibility that this oxide might in some way enhance carbon porosity. Two black-paint chars, WBBP-B and SBBP-A, showed a surface area close to that of coal-based IBC-109 char despite the differences in ash content. The chars produced from manufacturer B's black paints contained substantially higher ash content than those of IBC-109 and the Calgon carbons. The high ash contents of manufacturer B's black-paint chars (21% for WBBP-B and 59.3% for SBBP-B) were somewhat surprising because the major inorganic ingredient of paints was thought to come from pigments and the carbon-black pigment of the black paints should not be part of the ash. On the other hand, the ash contents of the white paints were high (over 80%), as expected, because of the incombustible white pigment, titanium dioxide.

The particle-size distributions of the chars were not determined. However, the black-paint chars were visually powdery and black and were similar to a typical powdered AC, whereas the white-paint chars were mostly powdery and grey but contained some granular materials which were generally smaller than the size of a typical granular AC such as Calgon F-400.

Adsorption of p-Nitrophenol on Activated Chars

Adsorption isotherms are frequently described with the Freundlich isotherm equation as shown below.

$$X = KC_{eq}^{\frac{1}{n}} \qquad (1)$$

where X is the amount of p-nitrophenol adsorbed (mg p-nitrophenol/g adsorbent);
Ceq is equilibrium concentration of p-nitrophenol (mg/L); and
K and n are coefficients.

A straight line results when equation 1 is plotted on a log-log scale or when the equation is transformed to the logarithmic form (equation 2) and plotted.

$$\log X = \log K + \frac{1}{n}\log C. \qquad (2)$$

The coefficient, K, is the amount adsorbed at Ceq = 1 mg/L (the intercept of the plot of equation 2) and 1/n is the slope of the line.

The Freundlich isotherm equation is strictly empirical and does not converge to Henry's law at low equilibrium concentration. Nevertheless it is useful for data analysis. For example, K in Eq. (1) gives a measure of adsorption capacity of an adsorbent, and 1/n is a measure of adsorption intensity (Adamson, 1967). In other words, higher values of K and 1/n indicate higher adsorption capacity and adsorption energy, respectively.

The results of the isotherm experiments on the activated chars are shown in Figure 3 along with those of the Calgon carbons. An isotherm for a granular activated carbon, Calgon F-400, was obtained from the literature (Kim and Cognata, 1990).

All isotherms were fitted to the Freundlich equation as shown in Figure 3, and the resulting coefficients are shown in Table 4. As mentioned earlier, the coefficient, K, is frequently used as a measure of adsorption capacity. However, the concentration of 1 mg/L, at which the values of K are determined, was not within the range of p-nitrophenol concentration studied here, and therefore the amounts adsorbed at 100 mg/L were used instead to compare adsorption capacities of the adsorbents. The amounts adsorbed at 100 mg/L can be obtained directly from Figure 3 or calculated using Eq. (1) and the values of K and n in Table 4. These amounts are shown in Table 3 in terms of both total weight and ash-free weight of an adsorbent. Several observations can be made from the results shown in Figure 3 and Tables 3 and 4."

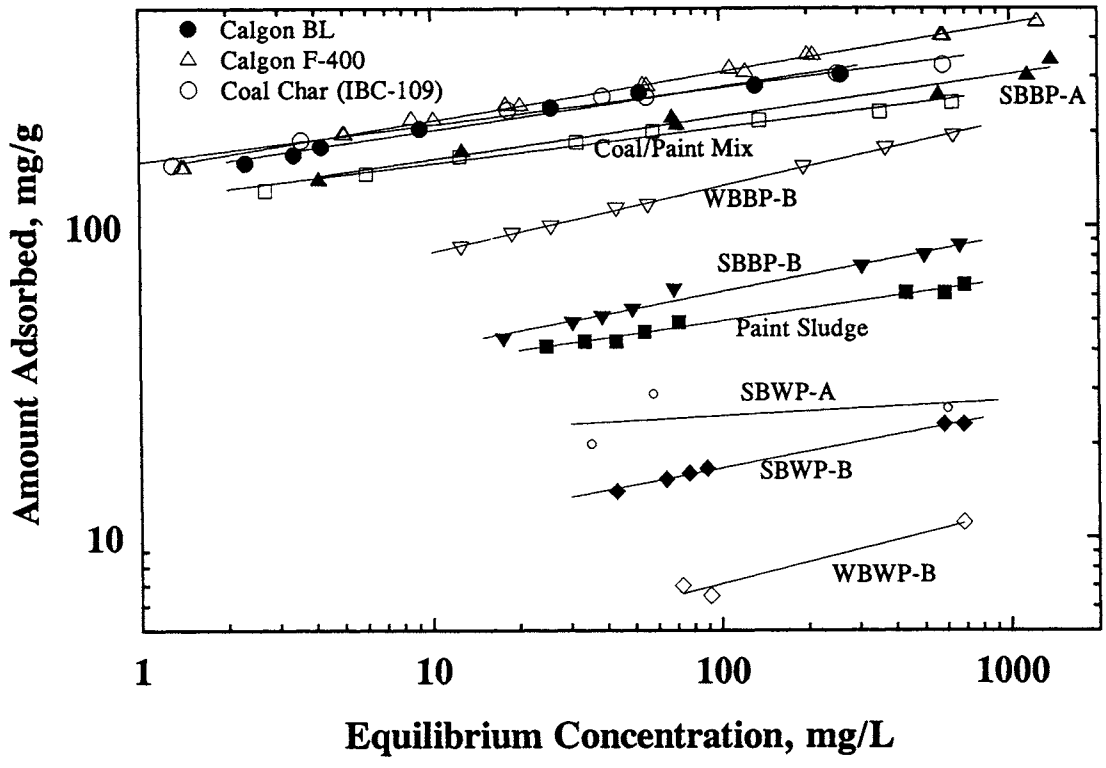

Figure 3: Adsorption of p-Nitrophenol on Activated Paint Chars and Activated Carbons

1. The adsorption capacities of the Calgon carbons (BL and F-400) and IBC-109 were comparable (see Figure 3 and Tables 3 and 4), even though the surface area of IBC-109 was much smaller than those of the commercially available Calgon carbons. This may be because the measurement of surface area was based on nitrogen and therefore cannot be directly applicable to the adsorption of p-nitrophenol. The Calgon carbons may have more micropores and a sizeable fraction of the surface area may not be accessible to p-nitrophenol molecules. However, the surface area is still a useful parameter for making a rough comparison among adsorbents.

2. The adsorption capacities of all the paint chars were always lower than those of the Calgon carbons and IBC-109. This might be related to the smaller surface area and high ash content only. One black-paint char, SBBP-A, had a high adsorption capacity, approximately 80% of the Calgon carbons.

Table 3: Surface Areas and Ash Contents of Activated Chars and Calgon Carbons

Adsorbents	Surface Area (m^2/g)		Adsorption Capacity at 100 mg/L of p-Nitrophenol (mg/g)		Ash Contents (%)
	Based on Total Weight	Based on Ash-Free Weight	Based on Total Weight	Based on Ash-Free Weight	
Calgon BL[1]	1,000-1,100	1,100-1,200	278	303	8.5 max.
Calgon F-400[2]	1,050-1200	-	311	-	not available
IBC-109	761	781	277	284	2.5
Coal-Paint Mix	576	627	206	224	8.1
Paint Sludge	205	594	49.6	144	65.5
WBBP-B	707	895	134	170	21.0
SBBP-B	236	580	61.6	151	59.3
SBBP-A	767	783	223	228	< 2[3]
WBWP-B	64	323	7.1	35.9	80.2
SBWP-B	83	565	16.7	114	85.3
SBWP-A	124	756	24.6	150	83.6

[1] Data in this table are from a Calgon Technical Bulletin
[2] Data in this table are from Calgon Activated Carbon Product Bulletin
[3] The ash content of a sample of SBBP-A, not used in this study, was only 1.7%. Based on that determination, the value reported in the table is less than 2%.

Table 4: Freundlich Parameters for Chars and Calgon Carbons

Adsorbents	n	K, (mg/g) $(mg/L)^{-1/n}$ or Adsorption Capacity at 1 mg/L of p-Nitrophenol (mg/g)
Calgon BL	7.19	147
Calgon F-400	6.43	152
IBC-109	8.45	160
Coal-Paint Mix	8.65	121
Paint Sludge	7.51	26.9
WBBP-B	4.75	50.7
SBBP-B	5.59	27.0
SBBP-A	7.37	120
WBWP-B	4.32	2.44
SBWP-B	5.65	7.39
SBWP-A	20.5	19.7

3. The adsorption capacities of the black-paint chars were higher than those of the white-paint chars. The white-paint chars had a smaller surface area and higher ash content than the black-paint chars. The low adsorption capacity of the white-paint chars indicates that the pigment, titanium dioxide, did not appreciably participate in the adsorption of a compound such as p-nitrophenol. It remains to be seen whether this is also true for the adsorption of more hydrophilic compounds such as alcohols.

4. It is quite interesting to note that the paint-sludge char, which was produced from a paint sludge collected at an automotive assembly plant, where a variety of paints was used, showed an adsorption capacity which was between those of the black-paint chars and those of the white-paint chars. The ash content of the paint-sludge char was between those of the two groups of chars. This seems to support the initial idea that black paints would produce adsorbents with relatively high adsorption capacity among a variety of paints whereas white paints would do the opposite. The adsorption capacity of the paint-sludge char is approximately 18% (total weight based) and 48% (ash-free weight based) of that of Calgon BL. This adsorption capacity is still substantial, and the idea of putting a paint-sludge char back into a scrubber for capturing paint VOCs from the spray-booth air seems promising.

5. The coal-paint mix char showed a high adsorption capacity indicating that the addition of coal to improve the quality of the resulting char and to reduce ash content is feasible. As mentioned earlier, the char was produced from a mixture of coal and the solvent-borne white paint (manufacturer B). A material balance calculation based on the ash contents of the IBC-109, the coal-paint mix and the SBWP-B, indicate coal-paint mix char was produced from 7% SBWP-B and 93% IBC-109. The projected adsorption capacity of coal-paint mix, using the calculated composition and the individual adsorption capacities of SBWP-B and IBC-109, is 259 mg/g (total weight based), shown in Table 3. This is higher than the experimental value, 206 mg/g (total weight based). The difference may be the result of some blockage of pores by the titanium dioxide.

6. The slopes of all the paint-char isotherms (1 divided by the n in Table 4) are close to those of the Calgon carbons and are relatively flat (i.e., n is much greater than 1). This means that the adsorption capacity of a paint-sludge char can be efficiently used even at relatively low concentrations. In addition, the similar slopes indicate that the Calgon carbons and the paint chars have similar surface characteristics in terms of their affinity for p-nitrophenol because the slope roughly represents the adsorption energy.

7. The adsorption capacity at 100 mg/L of p-nitrophenol, which is listed in Table 3, is plotted against surface area in Figure 4. Both the amount adsorbed and the surface area in the top figure are based on total weight of the eleven adsorbents, whereas those in the bottom figure are based on ash-free weight of the same adsorbents. The solid lines are linear regression lines. The results show that the adsorption capacity appears to increase linearly with the surface area.

With regard to the possibility of implementing this pyrolysis process at an automobile assembly plant, one major factor is the amount of paint sludge available at the plant for

conversion to activated char and what fraction of the plant's activated carbon requirement could be met with its own sludge-derived adsorbent. The amount of sludge available may prove be too small to justify a dedicated facility for each assembly plant for making activated carbon. If so, it might be more economical to build a relatively large, centralized facility to which several assembly plants could send their paint sludges. This might be particularly true for the southeast region of Michigan where many assembly plants are located. In addition, blending the sludge with coal as feed at this centralized facility may not only improve the adsorption capacity of the resulting char but may be justified to meet the market demand of the area. Factor to consider in selecting a location of a central facility will include the amount of coal to be used, the transportation cost of coal from its source to the plant, and the shipping costs both for shipping paint sludge from the assembly plants to the central facility and for the return shipment of the product char to the assembly plants. Rough calculation at one plant indicate the quantity of adsorbent needed is several fold greater than would be produced from sludge. If that be generally true, it could prove economically attractive to ship all of the paint sludge to a coal producing area, and manufacture the adsorbent there. Disposition or regeneration of the spent adsorbent is another question to be answered.

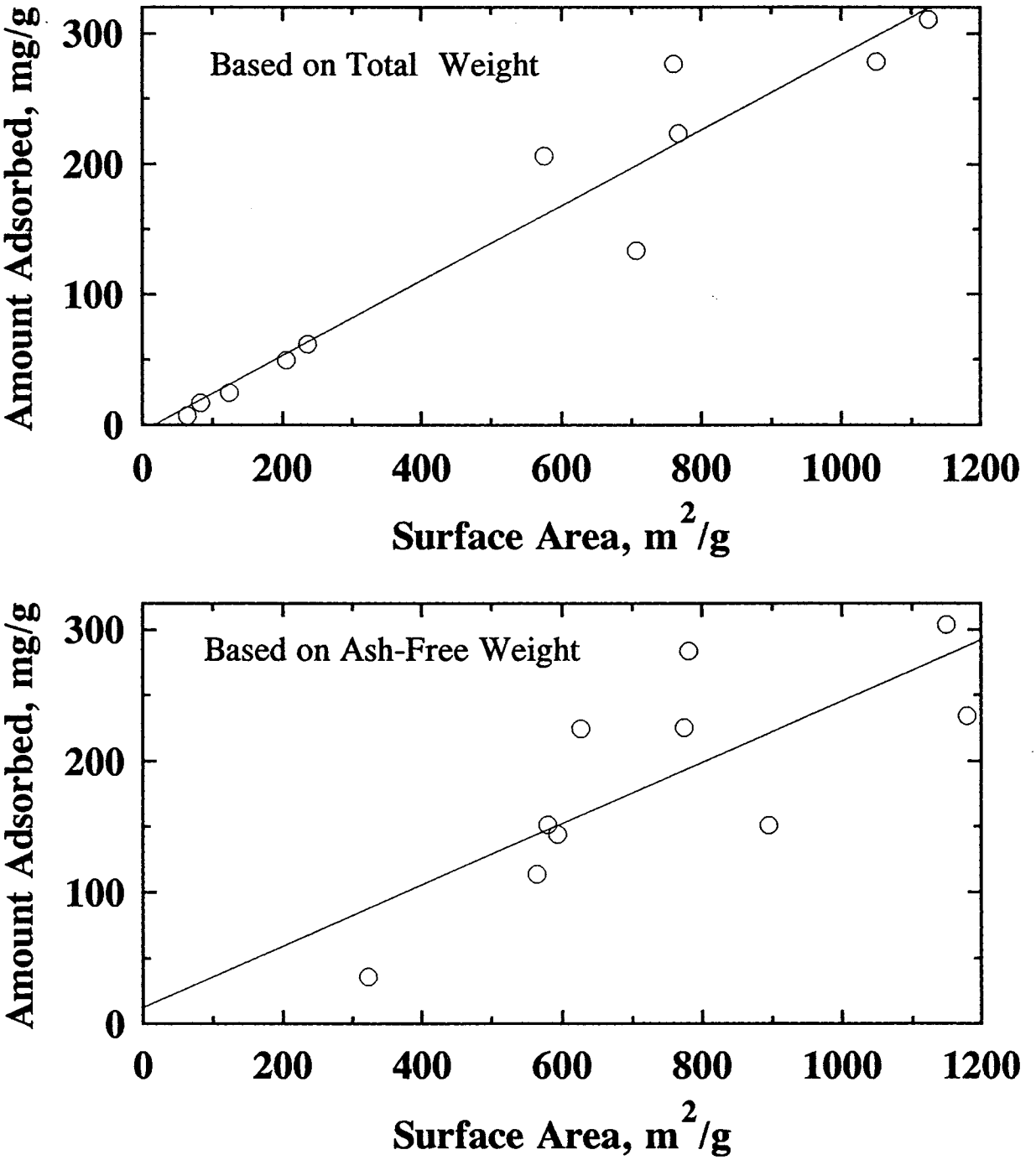

Figure 4: Effect of Surface Area of Char on the Adsorption Capacity for 100 mg/L of p-Nitrophenol

4.0 SUMMARY

The technical feasibility of producing activated carbon from real and simulated paint sludge was examined jointly by Ford Research Laboratory (FRL) and the Illinois State Geological Survey (ISGS). In this project, the ISGS produced nine chars using several dried paints, a paint sludge, a coal, and a coal-dried paint mixture. FRL conducted liquid-phase adsorption experiments using p-nitrophenol as an adsorbate to evaluate adsorption capacities of the chars and compared the results with those of commercially available activated carbons.

The primary findings are as follows:

- Unactivated paint chars had very little surface area and no appreciable capacity to adsorb p-nitrophenol. Activated carbons were produced from paint products by charring a 50:50 weight mixture of KOH and paint product and then carefully washing away the potassium hydroxide and other components solubilized by the strong base. Paint polymers being essentially the same, differences were not seen between solvent borne and water borne paints.

- The black-paint chars showed a substantially larger surface area than the white-paint chars, probably due to the white pigment, titanium dioxide, which is not expected to form a porous adsorbent material. Two black-paint chars, WBBP-B and SBBP-A, showed surface areas close to that of the IBC-109 char, an activated bituminous char produced under the same conditions as used for the black-paint chars.

- The black-paint chars, produced from manufacturer B's paints, showed unexpectedly high ash contents (21% for WBBP-B and 59.3% for SBBP-B) for a paint using carbon black as pigment.

- The ash content of the white-paint chars was very high (over 80%), as expected, because of the white pigment, titanium dioxide.

- The adsorption capacities of the Calgon carbons (BL and F-400) and IBC-109 carbon were comparable and were higher than those of the paint chars.

- The adsorption capacities of the black-paint chars were higher than those of the white-paint chars indicating that the pigment, titanium dioxide, did not participate appreciably in the adsorption of p-nitrophenol or in making the carbon structure more active.

- The paint-sludge char showed an adsorption capacity and an ash content between those of the black-paint chars and those of the white-paint chars, as expected from the fact that the sludge was formed from a variety of paints. The adsorption capacity of the paint-sludge char was found to be a little less than 20% (total weight based) and 50% (ash-free weight based) of the Calgon BL's.

- The fact that coal-paint mix char showed an adsorption capacity that was expected for the fraction of coal in the mix suggests that there is no synergism between the white

paint's titanium dioxide and coal for producing additional surface area or adsorption capacity. However, it was found that coal could be added to paint sludge to improve the quality of the resulting char and to reduce ash content.

- The slopes of the paint-char adsorption isotherms were close to those of the Calgon carbons and were relatively flat (i.e., n is much greater than 1), indicating that the adsorption capacity of a paint-sludge char could be efficiently used even at relatively low concentrations of p-nitrophenol.

- The adsorption capacity at 100 mg/L of p-nitrophenol was found to increase linearly with surface area.

- Chemical activation parameters were not optimized. A KOH/paint ratio other than 1/1 or the use of other chemical agents may improve the adsorption properties of chars derived from paint materials.

REFERENCES

Adamson, A.W. 1967. Physical Chemistry of Surfaces, 2nd edition. Interscience Publishers, a division of John Wiley & Sons, New York.

Berghoff, M. 1993. "DryPure Drying System to Process Waste Sludges." SAE Tech. Paper Ser. 930695, presented at 1993 SAE International Congress and Exposition, Detroit, MI.

Calgon Activated Carbon Product Bulletin 1068a. 1976.

Calgon Technical Bulletin Pulverized Activated Carbon. 23-1006.

Fritz, W. and Schlünder, E.U. 1981. "Competitive Adsorption of Two Dissolved Organics onto Activated Carbon - I. Adsorption Equilibria." Chem. Eng. Sci., 36, 721.

Weast, R.C. and Selby, S.M., eds. 1982. *Handbook of Chemistry and Physics*, 63rd edition, The Chemical Rubber Co., Cleveland, OH.

Jagtoyen, M., Thwaites, M., Stencel, J., Mcenaney, B., Derbyshire, F. 1992. "Adsorbent Carbon Synthesis from Coals by Phosphoric Acid Activation." Carbon, 30 (7), 1089-1096.

Kim, B.R. and Cognata, M.B. 1990. "PAC Addition as a Means of Regenerating GAC in a GAC Fluidized-Bed Reactor." Water Res., 24, 103.

Kim, B. R. and Pingel, L. J.. 1989. "Removal of Toluene from Air Using PAC/Water Slurry Reactor." J. Env. Eng., ASCE, 115, 1025.

Kim, B.R., Snoeyink, V.L., and Saunders, F.M. 1976. "Adsorption of Organic Compounds by Synthetic Resins." J. Water Pollut. Control Fed., 48, 120.

Kruse, C. W. and N. F. Shimp. 1981. "Removal of organic sulfur by low-temperature carbonization of Illinois coals." in Coal Processing Technology, Volume VII, "A Chemical Engineering Progress Technical Manual", AIChE, p. 124-134 (ISGS Reprint 1981E).

Kruse, C. W., N. F. Shimp, R. J. Helfinstine and J. D. Cooper. 1988. "Low-sulfur fuels from coals. U.S. Patent 4,758,331, July 19.

Snoeyink, V. L., Weber, W. J., Jr., and Mark, H. B. 1969. Sorption of Phenol and Nitrophenol by Active Carbon. Envir. Sci. & Tech., 3, 918.

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Use of Char for Management of Paint Processing Waste

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ABSTRACT

Volatile organic compounds (VOCs) and paint sludge are generated by painting operations at automobile assembly plants. This study's goal was to demonstrate that paint sludge can be converted to adsorbents for the capture of VOCs. Combining coal with paint sludge was projected to improve the adsorbent quality and might improve economics show a significant "economy of the scale of operation". The Illinois State Geological Survey (ISGS) made a series of activated carbons from 1) dried paints, 2) overspray paint materials captured at an assembly plant, 3) coal and 4) with mixtures of paint products with coal. Adsorption capacities of the ISGS carbons were determined in the Ford Research Laboratory with p-nitrophenol as a model adsorbate.

Char making, or carbonization as it is often called, is the very old process of heating an organic substance in the absence of air to drive off the noncarbon components, primarily compounds of oxygen and hydrogen. Carbohydrates (a shortened version of carbon hydrates) derive their name from the early observation that they leave carbon when dehydrated by heating in the absence of air or by chemical agents such as sulfuric acid. Organic substances that do not melt, such as wood or nut hulls, produce a porous charcoal of the type marketed for use in home cooking grills. Removing carbon from a char by gasification enlarges the pore sizes and alters the pore size distribution resulting in activated carbons that have high internal surface areas. These activated carbons or those produced by chemical activation are the materials used in adsorption processes.

Initial charring of dry paint demonstrated that the product was not a carbon with appreciable surface area. Additionally the paint material went through a melting stage during charring. ISGS researchers turned then to chemical activation with potassium hydroxide (KOH) as a means of making an activated product. Properties of the control char derived from Illinois coal approximated those of Calgon Corporation commercial carbons. Carbon black and titanium dioxide (TiO_2) are pigments in automotive black and white paints, respectively. White paints generally have much higher ash contents than black paints. The ash content of black paints from the two manufacturers in this study were quite different suggesting some noncarbon black pigment was used. The lower the ash content of the adsorbents made, i.e. the more carbon, the better were the adsorbent properties. There was no evidence that ash-forming materials assisted in pore development. The quality of sludge-derived adsorbent was between those of adsorbents derived from black and white paints. Blending coal with white paint improved the adsorption capacity of adsorbent.

The results of the tests completed on the adsorbents made in this study warrant further study, both technical and economic. Tests using p-nitrophenol to compare adsorption properties of paint-derived adsorbents with those of commercially available adsorbents are being extended at Ford to include selected paint solvents. Confirmation at this level may justify larger scale production of the adsorbents for testing at a scale that provides information useful for preliminary economic calculations.

EXECUTIVE SUMMARY

Automotive painting operations generate a variety of wastes, primarily volatile organic compounds and paint sludge. The objectives of this study were: 1) to produce carbon-based adsorbent materials from dried paint materials and 2) to compare the adsorption capacities of the adsorbents produced from paint and paint sludges, or from mixtures of paint with coal, to those of commercially available adsorbent. Chars were chemically activated during pyrolysis by using potassium hydroxide (KOH).

The technical feasibility of producing activated carbon (AC) from real and simulated paint sludge was examined jointly by the Ford Research Laboratory (FRL) and the Illinois State Geological Survey (ISGS). The ISGS produced nine powdered activated chars (carbons) using several dried paints, a paint sludge, a coal, and a mixture of coal and dried paint. A pelletization step will likely be required to convert the powder to granular activated carbon (GAC), the physical form used in most systems adsorbing VOCs from gaseous streams. FRL conducted liquid-phase adsorption experiments using p-nitrophenol as the adsorbate to evaluate adsorption capacities of the chars and to compare the results with those obtained using commercially available activated carbons.

The primary findings were:

- Nonactivated paint chars had very little surface area and no appreciable capacity to adsorb p-nitrophenol. Activated carbons were produced from paint products by first charring a 50:50 weight mixture of KOH and paint product, and then washing away the potassium hydroxide and other components solubilized by the strong base.

- Activated black-paint chars showed substantially larger surface area than white-paint chars, probably due to the white pigment, titanium dioxide, which is not expected to form a porous adsorbent material. Two black-paint chars, WBBP-B and SBBP-A, showed a surface area close to that of an activated char made from a bituminous coal in the Illinois Basin Coal Sample Program (IBC-109) using the same conditions as used for the black-paint chars.

- Activated black-paint chars, produced from manufacturer B's paints, showed unexpectedly high ash contents (21% for WBBP-B and 59.3% for SBBP-B) for a paint using carbon black as pigment.

- The ash content of the white-paint chars was very high (over 80%), as expected because of the white pigment, titanium dioxide.

- The adsorption capacities of the Calgon carbons (BL and F-400) and the IBC-109 carbon were comparable to each other and higher than those of the paint chars.

- The adsorption capacities of the black-paint chars were higher than those of the white-paint chars indicating that the pigment, titanium dioxide, did not participate appreciably in the adsorption of p-nitrophenol or in making the carbon portion or the structure more active.

- The paint-sludge char showed an adsorption capacity and an ash content between those of the black-paint chars and the white-paint chars, as expected for a sludge formed from a variety of paints. The adsorption capacity of the paint-sludge char was found to be a little less than 20% (total weight based) and 50% (ash-free weight based) of the Calgon BL's.

- The fact that coal-paint mix char showed adsorption capacities that are expected for the fraction of coal in the mix suggests that there is no synergism between the white paint's titanium dioxide and coal for producing additional surface area or adsorption capacity. However, it was found that coal could be added to paint sludge to improve the quality of the resulting char and to reduce ash content.

- The slopes of the paint-char adsorption isotherms were close to those of the Calgon carbons and were relatively flat (i.e., n is much greater than 1), indicating that the adsorption capacity of a paint-sludge char could be efficiently used even at relatively low concentrations of a compound such as p-nitrophenol.

- The adsorption capacity at 100 mg/L of p-nitrophenol was found to increase linearly with surface area.

- Chemical activation parameters were not optimized. A KOH/paint ratio other than 1/1 or the use of other chemical agents may improve adsorption properties of chars derived from paint materials.

1.0 INTRODUCTION

During automotive spray-painting operations, the spray-booth air goes through a water scrubber to capture overspray paint particulates. Since the scrubber was not designed for the purpose of removing volatile organic compounds (VOCs) from the booth air, a significant portions of the paint solvents escape the scrubber. Therefore, the spray-painting operations generate wastes in gaseous, liquid, and solid phases: 1) VOCs emitted in stack air; 2) spent spray-booth scrubber water that contains some dissolved VOCs; and 3) paint sludge that results from the accumulation of the captured paint particulates. Currently at automotive assembly plants, gaseous emissions in the booth air of automatic spraying sections are controlled by using a vapor-phase activated carbon adsorption/incineration system to remove VOCs. The spent scrubber water is periodically discharged to a municipal wastewater treatment plant. The paint sludge is landfilled. The study reported herein addresses the solid wastes (paint sludge) as part of an effort to explore the possibility of recycling a processed paint sludge that by converting it to an adsorbent for the VOCs. There are several types of commercially available vapor phase adsorption systems. The one being used at Ford plants is based on a rotary adsorber that contains activated carbon fiber. This adsorber goes through continuous adsorption/desorption cycles as it rotates. This system is just one of many vapor phase adsorption systems. Identifying precisely the fate of the spent coal/paint char, i.e, whether it would be discarded or regenerated, was beyond the objectives of this preliminary study. While recovery of the VOCs for reuse appears to be an attractive possibility, the technical feasibility must be determined. Chemical interaction of different VOCs of various types make it less likely that recovery will be feasible. There have already been unsuccessful attempts to recover VOCs from some of the vapor phase adsorption systems.

One of the major factors that affects the costs of handling and disposing of paint sludge is the volume of the sludge. In order to reduce sludge volume, some automotive assembly plants have been drying the sludge. This reduces transportation and disposal costs and might make it possible to reuse the dried sludge for filler or to make low-quality paints (Berghoff, 1993).

Another process that could be used to reduce sludge volume is pyrolysis. The pyrolysis of paint sludge not only results in a smaller volume than that achieved by drying, but under some conditions could produce an activated char that could be used as an adsorbent. This pyrolysis and the subsequent use of the resulting char in a spray-booth scrubber would have dual benefits. First, the volume reduction is expected to be much more than that by drying alone because the pyrolysis of paint sludge not only removes moisture but also breaks down organic matter. Secondly, the pyrolysis of paint sludge coupled with an activation step can produce activated carbon, which can be put back into the scrubber water as an adsorbent to remove VOCs (especially nonpolar VOCs) from the booth exhaust air. Kim and Pingel (1989)

experimentally and mathematically showed that toluene was effectively removed from air using a powdered activated carbon/water slurry in a reactor.

In order to examine the technical feasibility of producing activated carbon from paint sludge, a joint research program was developed between Ford Research Laboratory (FRL) (Dearborn, Michigan) and the Illinois State Geological Survey (ISGS) (Champaign, Illinois). In this program, the ISGS was responsible for producing and characterizing chars from paints, paint sludge, and a mixture of paint with coal. FRL was responsible for supplying the paint materials and performing adsorption studies with the chars. The ISGS supplied nine chars derived from six dried paints (simulated paint sludges), a paint sludge, a coal, and a coal/paint mixture. FRL conducted liquid-phase adsorption experiments to evaluate adsorption capacities of the chars and compared the results with those of commercially available activated carbons. The adsorbate selected for this study, p-nitrophenol, has been frequently used as a model adsorbate by many researchers in the environmental field (Snoeyink et al., 1969; Kim et al., 1976; Fritz and Schlunder, 1981; Kim et al., 1990; Kim and Cognata, 1990). The use of this adsorbate facilitates comparisons of the adsorption properties of adsorbents made in this study with those reported in the literature. Although a direct relationship is not expected between the adsorption capacities for p-nitrophenol and paint solvents on two adsorbents, two adsorbents with comparable capacities for p-nitrophenol are likely to exhibit comparable capacities for paint solvents in a general sense.

2.0 MATERIALS AND METHODS

2.1 Materials

The adsorbents used in this study are listed in Table 1. The table includes the base materials used (coal, paint sludge, and paints), the nature of solid materials in paints, and the sources of the paint materials. Calgon F-400 (Calgon Corp., Pittsburgh, Pennsylvania) was not used in this study. However, a set of adsorption data on the F-400 carbon was obtained from the literature (Kim and Cognata, 1990) and was used for data analysis. Calgon BL and F-400 are similar except in particle size (Calgon, 1976; Calgon, undated).

Six paints were obtained from two paint manufacturers: two solvent-borne paints (black and white) from manufacturer A; two solvent-borne paints (black and white) from manufacturer B; and two water- borne paints (black and white) from manufacturer B. According to Material Safety Data Sheets, all paints contained a melamine-formaldehyde resin and other resins. The black paints contained carbon black as a pigment whereas the white paints contained titanium dioxide as a pigment.

The paint sludge was obtained from an assembly plant in a dry form. In that plant, overspray paint materials were captured using a wet scrubber, detackified (made nonsticky) using organic polymers, collected through flotation, and dried using a thermal dryer.

The coal was the Herrin (Illinois No. 6) coal from lot IBC-109 in the Illinois Basin Coal Sample Program. The program is sponsored by the Illinois Department of Energy and Natural Resources through its Coal Development Board and the Illinois Clean Coal Institute. The coal sample bank is located at the ISGS. Lot IBC-109 is a low sulfur Illinois coal. Its total sulfur content of 1.2% is low enough to permit making metallurgical grade coke from this coal. The coal-derived char served as a control with which to compare the properties of chars made from the coal/paint mix, the dried paints, and the paint sludge and also those of commercially available activated carbons.

The coal-paint-mix char was prepared by mixing the Illinois coal (IBC-109) with a solvent-borne white paint (manufacturer B) prior to pyrolysis.

p-Nitrophenol (99+%) was obtained from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. The pKa of p-nitrophenol is 7.15 (Weast and Shelby, 1982). Reagent-grade potassium hydroxide (85.0% minimum assay) was obtained from EM Science, a Division of EM industries, Inc. and an associate of E. Merck, Darmstadt, Germany. The weight ratios used to describe KOH activation were based on the total reagent weight, not the KOH content of the material. Reagent-grade concentrated

Table 1: Adsorbents Used in This Study

Adsorbents		Base Materials	Solids in Paints	Sources
Name	Type			
Calgon BL	PAC[1]	Bituminous Coal	-	Calgon Corp.
Calgon F-400	GAC[2]	Bituminous Coal	-	Calgon Corp.
IBC-109	Coal Char (activated)	Bituminous Herrin (Illinois No. 6) Coal	-	Southern Illinois preparation plant
Coal-Paint Mix	Coal-Paint Mix Char (activated)	A Mixture of Illinois No. 6 Coal and Dried Solvent-borne White Paint	melamine-formaldehyde polymer, polyurethane polymer, titanium dioxide	Southern Illinois preparation plant/ Paint Manufacturer B
Paint Sludge	Paint-Sludge Char (activated)	Dried Paint Sludge	Unknown (a mixture of many paints)	An Automotive Plant
WBBP-B	Black-Paint Char (activated)	Dried Water-borne Black Paint	melamine-formaldehyde polymer, polyurethane polymer, carbon black	Paint Manufacturer B
SBBP-B	Black-Paint Char (activated)	Dried Solvent-borne Black Paint	melamine-formaldehyde polymer, polyurethane polymer, carbon black	Paint Manufacturer B
SBBP-A	Black-Paint Char (activated)	Dried Solvent-borne Black Paint	butylester polymer, melamine-formaldehyde polymer, polyester polymer, carbon black	Paint Manufacturer A
SBBP-A-N	Black-Paint Char (nonactivated)	same as above	same as above	Paint Manufacturer A
3WBWP-B	White-Paint Char (activated)	Dried Water-borne White Paint	melamine-formaldehyde polymer, polyurethane polymer, titanium dioxide	Paint Manufacturer B
SBWP-B	White-Paint Char (activated)	Dried Solvent-borne White Paint	melamine-formaldehyde polymer, polyurethane polymer, titanium dioxide	Paint Manufacturer B
SBWP-A	White-Paint Char	Dried Solvent-borne White Paint	ethylester polymer, melamine-formaldehyde polymer, titanium dioxide, silica	Paint Manufacturer A

[1] Powdered Activated Carbon
[2] Granular Activated Carbon

hydrochloric acid fromFisher Scientific, Fair Lawn, New Jersey, was diluted with deionized water to prepare a 5N solution used to wash the chars. Deionized water was used in all adsorption experiments.

2.2 Analytical Methods

The surface areas of the chars were measured with a Quantachrome Monosorb Surface Area Analyzer produced by the Quantachrome Corporation, Syosset, New York. The Monosorb uses the single point Brunauer, Emmet, and Teller (BET) method for calculating the surface area from the amount of nitrogen adsorbed at −196°C by a sample that has been degassed at 130°C under vacuum prior to introduction of the adsorbate nitrogen.

A Cahn TG-131 thermogravimetric analyzer manufactured by the Cahn Corporation located in Cerritos, California, was used to determine the volatile matter and ash of the samples. The program provided for the determination of weight loss on heating to 950°C at 50°C/min in nitrogen. After holding the devolatilized material at 950°C for 3 minutes, the ash content was determined after cooling down to 750°C and burning the carbon away in air flowing at 100 mL/min.

The concentration of p-nitrophenol was measured using a Lambda 6 UV/visible spectrophotometer (The Perkin-Elmer Corporation of Oakbrook, Illinois) at a wavelength of 317 nm. An ion analyzer Model 960 (Orion Research, Cambridge, Massachusetts) was used to measure pH.

2.3 Experimental Methods

Preparation of Base Materials for Pyrolysis. Each paint was separately dried at FRL by heating it at approximately 50°C in a hood for several weeks until most of the paint solvents evaporated, and then placing it in an oven at approximately 110°C for several days. The paint was further dried at ISGS in a vacuum oven (a Lab-line Duo-Vac oven manufactured by Lab-Line Inst. Inc. in Melrose Park, Illinois) at approximately 100°C under vacuum for approximately two days. Before the vacuum drying, each dried paint was crushed to 16 mesh or smaller, a size suitable for the vacuum drying oven. The "bowl" of the hand-operated crusher was a cup formed by welding a 10 in. (25.4 cm) cylindrical section of 8 in. (20.3 cm) pipe to a heavy-gauge steel plate. The crusher (pestle) was a 25 lb (11.4 kg) disk (1 in. [2.54 cm] thick x 5 in. [12.7 cm] diameter) attached to a T-shaped, 30 in. (76.2 cm) handle suitable for applying pressure and torque from a standing position. Crushing of tarry or spongy paint samples was time-consuming, but it was facilitated by cooling them in liquid nitrogen before crushing. The coal was ground to minus 60 mesh particle size in Model 500 mill manufactured by Holmes Brothers Inc., Danville, Illinois. Neither the coal nor the paint sludge required the vacuum drying.

Pyrolysis. Two pyrolysis methods were used: 1) small-scale charring for initial scoping tests and 2) continuous-feed charring for producing larger amounts of chars. The small-scale charring was carried out under a nitrogen atmosphere (1 liter/minute) in a 1400-W furnace (a Lindberg-type 54232 tube furnace with a Lindberg-type 59344 controller from Lindberg Corporation in Watertown, Wisconsin), which was fitted with a 34 in. (86.4 cm) long by 1.5 in. (3.81 cm) ID mullite tube. A ceramic boat was loaded with a prepared base material, and pushed into the heated zone of the furnace for the desired residence time and then moved to the section of the furnace extending beyond the heated zone to cool. The paints from manufacturer A were pyrolyzed using this method.

The continuous-feed charring was conducted in a continuous-feed charring oven (CFCO), which was patterned after one designed and built at ISGS for thin bed charring of coal (Kruse and Shimp, 1981; Kruse et al., 1988). The char production rate of the CFCO was 100 g per hour. A drawing of the CFCO is shown in Figure 1. A belt of overlapping, stainless steel trays, forming a 5.5 in. (14.0 cm) wide trough, carries the material to be charred through the electrically-heated charring zone. The CFCO can be used at temperatures up to 700°C. The bed depth can be varied from around 1/10 in. (0.25 cm) to 3/4 in. (1.91 cm). The range of residence time is generally from 5 to 45 minutes. The temperature in the oven is regulated by programmable temperature controllers on the heating rods above and below the conveyor belt. The feeder has a slide that is used to regulate the depth of the material on the conveyor. A variable speed motor driving the conveyor regulates residence times in the heated zone. The housing maintains a nitrogen atmosphere in the oven. The nitrogen flows counter to the direction the conveyor belt moves. As the material passes through a heating zone of successively higher temperatures the inert gas removes volatile pyrolysis products to a lower temperature zone insuring that the pyrolysis products do not react with char that has reached a higher temperature. The CFCO was used to produce all activated chars from the coal-paint mix, the paint sludge, and the paints from both manufacturers.

Chemical Activation. Chemical activation was used to increase the surface area of the resulting chars. Except for the coal-paint mix, the base material was mixed with KOH at a weight ratio of 1 to 1 prior to pyrolysis. The weight of KOH was based on the total weight of KOH pellets, not their assayed KOH content. The addition of water and a small amount of detergent facilitated mixing. The detergent used was Alconox made by Alconox, Inc. located in New York City, New York. Most of the added water was removed in the subsequent drying step in which the mixture of KOH and a base material (paint-derived) was occasionally stirred at approximately 100°C for two days under reduced pressure. The dried mixture was pyrolyzed at 600°C for 30 minutes in a nitrogen atmosphere in the CFCO. The pyrolyzed paint/KOH mixture was washed with warm deionized water to remove most of the KOH. It was then soaked in 5N HCl for 15 hours, and washed again with deionized water. The chars were dried at approximately 110°C and stored in a desiccator prior to use.

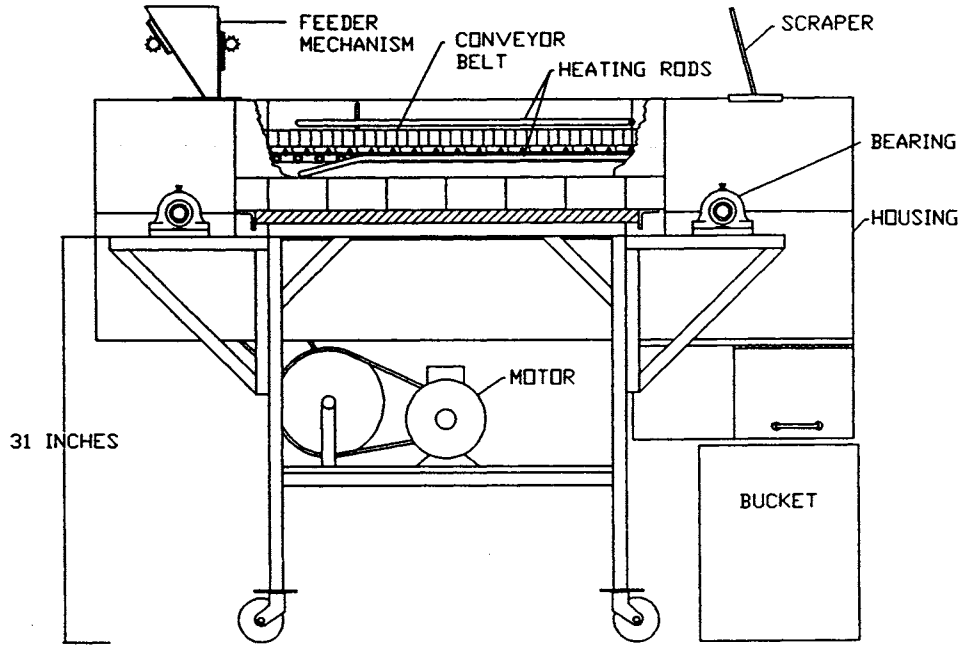

Figure 1: Thin Bed, Continuous-Feed, Charring Oven (CFCO) with Cut Away View of Reactor

The procedure for preparing a coal-paint mix adsorbent involved two mixing steps prior to pyrolysis. A paint/KOH mixture and a coal/KOH mixture were prepared separately and then mixed to yield a coal-to-paint ratio of 9 to 1. The paint/KOH mixture was 1 part solvent-borne white paint (manufacturer B) with 1 part KOH, whereas the coal/KOH mixture was 1 part Illinois coal with 1.5 parts KOH.

Isotherm Experiments. Isotherm experiments were conducted in 250 mL or 125 mL amber glass bottles with Teflon-lined caps. Two or three glass beads approximately 1/8" in diameter were added to each bottle to aid in mixing. Each bottle was prepared by adding predetermined amounts of an adsorbent and filled with a p-nitrophenol solution of a known concentration. Then the bottles were packed into paint cans which were placed on a roller apparatus (Bellco Glass, Vineland, New Jersey) for mixing. After at least four days of mixing for equilibration, the bottles were centrifuged prior to analysis to remove adsorbent particles using a Sorvall RB-5C Superspeed Centrifuge (Du Pont Instruments, Newtown, Connecticut)

All isotherm experiments were conducted at room temperature (21 to 25°C) and at a pH less than 4 to ensure that p-nitrophenol was in the neutral form. A dilute H_2SO_4 solution was used for pH control.

3.0 RESULTS AND DISCUSSION

3.1 Initial Scoping Tests

Initially, the two paints (black and white) from manufacturer A were used to determine whether activation was needed to increase surface area and what type of activation was needed. The selection of these two paints was made based on their pigments (carbon black for the black paint and titanium dioxide for the white paint) to represent two extreme types of paints with regard to their potential ash content after pyrolysis. The moisture-free analyses of the paints confirmed that the white paint had a much higher ash content (24.7%) and a lower fixed carbon content (2.9%) than those of the black paints (0.05% and 4.7%, respectively). With this information, it was concluded that the black paint would result in an adsorbent with a higher surface area than the white paint. Therefore, the pyrolysis of the black paint was conducted with and without activation. The surface areas of both activated and nonactivated char are shown in Table 2 along with those of Calgon BL, Calgon F-400 and an Illinois coal for comparison. The Calgon carbons had higher surface areas than those of the activated paint or coal chars. The nonactivated char had no appreciable surface area.

Table 2: Surface Areas of Activated and Nonactivated Chars and Calgon Carbons

Adsorbents	Surface Area, m^2/g
Calgon BL[1]	1,000-1,100
Calgon F-400[2]	1,050-1,200
SBBP-A-N (Nonactivated Char)	19
SBBP-A (Activated Char)	767
IBC-109 (Activated coal char)	761

[1] Powdered Activated Carbon
[2] Granular Activated Carbon

Adsorption capacities of the chars were also compared with those of Calgon carbons as shown in Figure 2. Because Calgon F-400 has been widely used and tested by many researchers for removing organics from water, it was used as a second reference adsorbent. Only one isotherm point was obtained for the nonactivated char because the amount of p-nitrophenol adsorbed was too small to measure even with high adsorbent dosages of 0.5 g/L to 1.3 g/L. The results of the adsorption experiments clearly showed that 1) the adsorption capacity of the

nonactivated char for p-nitrophenol was insignificant due to the very low surface area; 2) the adsorption capacity of the activated char was comparable to those of commercially available activated carbons; and 3) an activation step was needed if chars from paint materials were to be used as adsorbents.

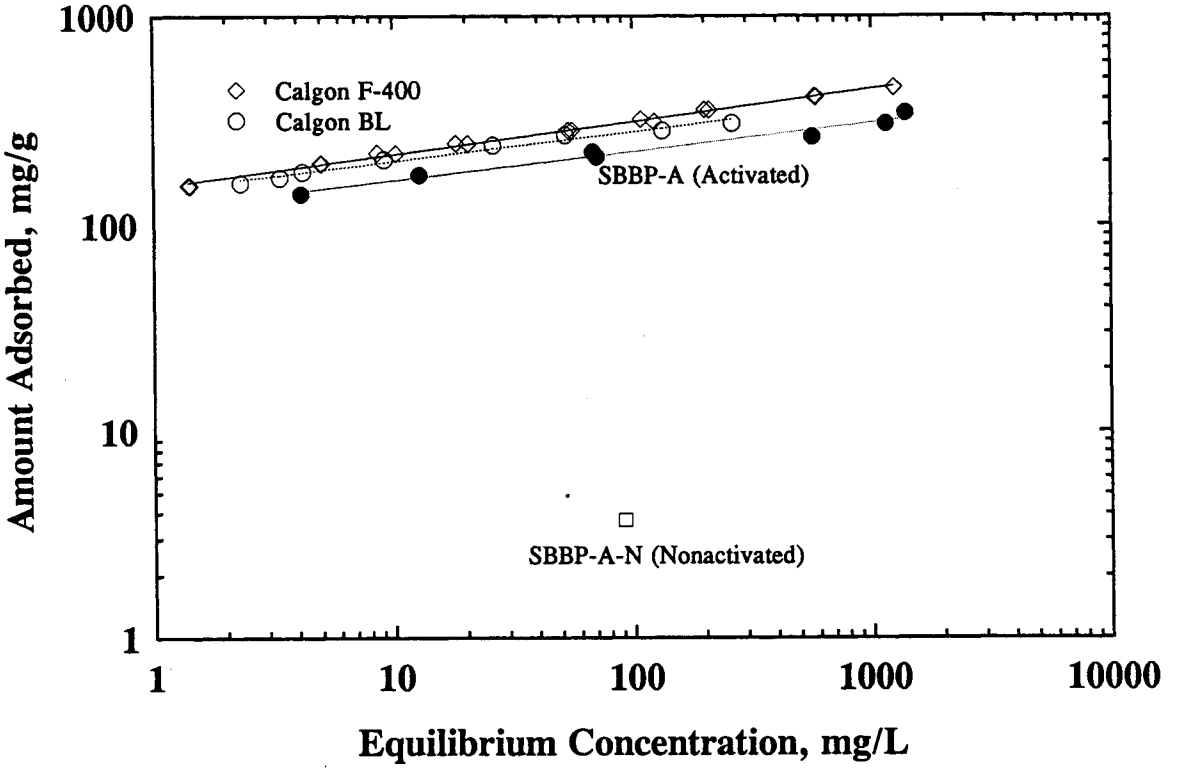

Figure 2: Adsorption of p-Nitrophenol on SBBP-A (Activated), SBBP-A (Nonactivated), and Activated Carbons

Typically, activated carbon is produced from a base material in a fluidized bed through a pyrolysis step under reducing conditions (e.g., under a nitrogen atmosphere) followed by an activation step in the presence of a small amount of oxygen (e.g., 1 % oxygen in high purity nitrogen). In the activation step, some easily oxidizable portions of the charred material are oxidized, resulting in a more porous structure, thus higher surface area. However, this two-step process was found to be inapplicable because initial tests using the small-scale charring oven showed that the paints melted before losing appreciable volatile matter. Therefore, a one-step process, in which pyrolysis

and chemically-aided activation take place simultaneously in a fixed bed, was chosen for this study.

KOH was used for activation in this process. The charred solvent-borne black paint (SBBP-A-N) had a nitrogen surface area of only 19 m^2/g. When ten percent KOH raised the surface area to only 128 m^2/g, the KOH percentage was raised to 50%. Values of 718 and 767 m^2/g were obtained in two tests. The sample with the higher surface area was used for adsorption tests. The process of activation was not optimized. A KOH/paint ratio other than one to one weight ratio or the use of other chemical agents such as phosphoric acid may improve adsorption properties of chars derived from paint materials over those reported (Jagtoyen et al., 1992).

3.2 Physical Characteristics of Activated Chars

The BET nitrogen surface areas of the activated chars were calculated on both a total weight basis and an ash-free weight basis. The results are shown in Table 3 along with the Calgon carbons. The Calgon carbons had higher surface areas than those of the chars prepared for this study including the two in which the Illinois coal was used (IBC-109 and coal-paint mix). The black-paint chars had substantially higher surface areas than the white-paint chars. This was expected because the main pigment used in the white paints is titanium dioxide. Titanium dioxide was not expected to form a porous material although there was the possibility that this oxide might in some way enhance carbon porosity. Two black-paint chars, WBBP-B and SBBP-A, showed a surface area close to that of coal-based IBC-109 char despite the differences in ash content. The chars produced from manufacturer B's black paints contained substantially higher ash content than those of IBC-109 and the Calgon carbons. The high ash contents of manufacturer B's black-paint chars (21% for WBBP-B and 59.3% for SBBP-B) were somewhat surprising because the major inorganic ingredient of paints was thought to come from pigments and the carbon-black pigment of the black paints should not be part of the ash. On the other hand, the ash contents of the white paints were high (over 80%), as expected, because of the incombustible white pigment, titanium dioxide.

The particle-size distributions of the chars were not determined. However, the black-paint chars were visually powdery and black and were similar to a typical powdered AC, whereas the white-paint chars were mostly powdery and grey but contained some granular materials which were generally smaller than the size of a typical granular AC such as Calgon F-400.

Adsorption of p-Nitrophenol on Activated Chars

Adsorption isotherms are frequently described with the Freundlich isotherm equation as shown below.

$$X = KC_{eq}^{\frac{1}{n}} \qquad (1)$$

where X is the amount of p-nitrophenol adsorbed (mg p-nitrophenol/g adsorbent);
Ceq is equilibrium concentration of p-nitrophenol (mg/L); and
K and n are coefficients.

A straight line results when equation 1 is plotted on a log-log scale or when the equation is transformed to the logarithmic form (equation 2) and plotted.

$$\log X = \log K + \frac{1}{n}\log C. \qquad (2)$$

The coefficient, K, is the amount adsorbed at Ceq = 1 mg/L (the intercept of the plot of equation 2) and 1/n is the slope of the line.

The Freundlich isotherm equation is strictly empirical and does not converge to Henry's law at low equilibrium concentration. Nevertheless it is useful for data analysis. For example, K in Eq. (1) gives a measure of adsorption capacity of an adsorbent, and 1/n is a measure of adsorption intensity (Adamson, 1967). In other words, higher values of K and 1/n indicate higher adsorption capacity and adsorption energy, respectively.

The results of the isotherm experiments on the activated chars are shown in Figure 3 along with those of the Calgon carbons. An isotherm for a granular activated carbon, Calgon F-400, was obtained from the literature (Kim and Cognata, 1990).

All isotherms were fitted to the Freundlich equation as shown in Figure 3, and the resulting coefficients are shown in Table 4. As mentioned earlier, the coefficient, K, is frequently used as a measure of adsorption capacity. However, the concentration of 1 mg/L, at which the values of K are determined, was not within the range of p-nitrophenol concentration studied here, and therefore the amounts adsorbed at 100 mg/L were used instead to compare adsorption capacities of the adsorbents. The amounts adsorbed at 100 mg/L can be obtained directly from Figure 3 or calculated using Eq. (1) and the values of K and n in Table 4. These amounts are shown in Table 3 in terms of both total weight and ash-free weight of an adsorbent. Several observations can be made from the results shown in Figure 3 and Tables 3 and 4."

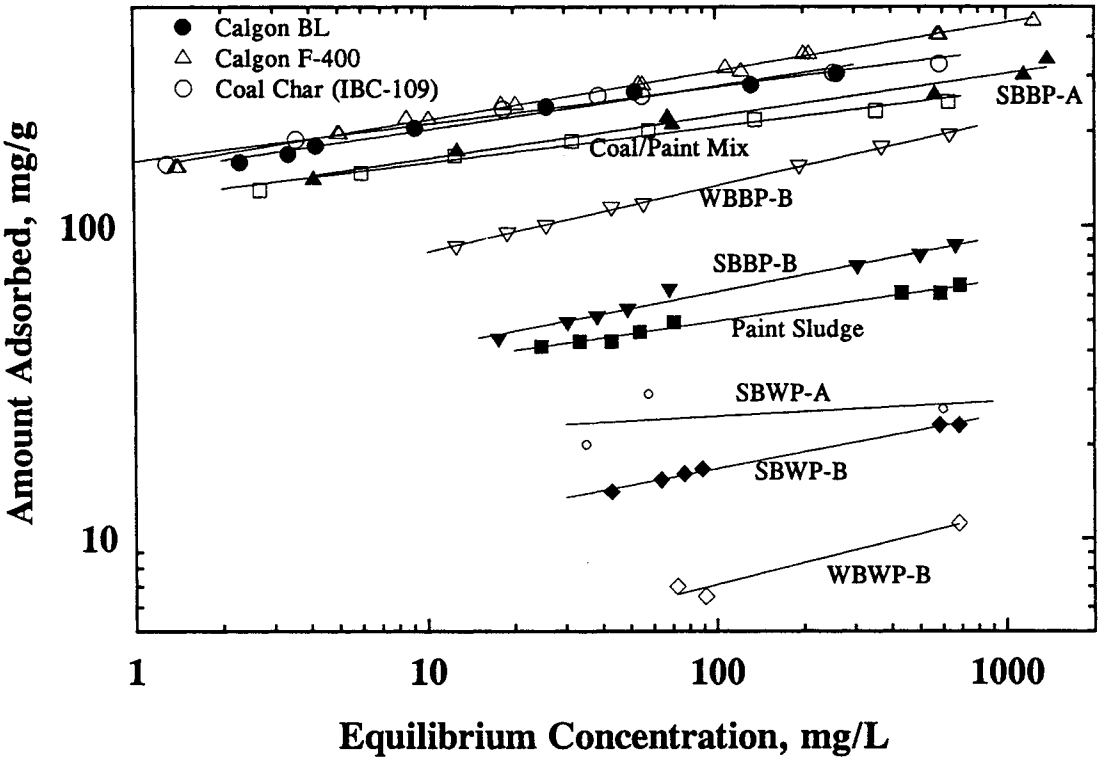

Figure 3: Adsorption of p-Nitrophenol on Activated Paint Chars and Activated Carbons

1. The adsorption capacities of the Calgon carbons (BL and F-400) and IBC-109 were comparable (see Figure 3 and Tables 3 and 4), even though the surface area of IBC-109 was much smaller than those of the commercially available Calgon carbons. This may be because the measurement of surface area was based on nitrogen and therefore cannot be directly applicable to the adsorption of p-nitrophenol. The Calgon carbons may have more micropores and a sizeable fraction of the surface area may not be accessible to p-nitrophenol molecules. However, the surface area is still a useful parameter for making a rough comparison among adsorbents.

2. The adsorption capacities of all the paint chars were always lower than those of the Calgon carbons and IBC-109. This might be related to the smaller surface area and high ash content only. One black-paint char, SBBP-A, had a high adsorption capacity, approximately 80% of the Calgon carbons.

Table 3: Surface Areas and Ash Contents of Activated Chars and Calgon Carbons

Adsorbents	Surface Area (m^2/g)		Adsorption Capacity at 100 mg/L of p-Nitrophenol (mg/g)		Ash Contents (%)
	Based on Total Weight	Based on Ash-Free Weight	Based on Total Weight	Based on Ash-Free Weight	
Calgon BL[1]	1,000-1,100	1,100-1,200	278	303	8.5 max.
Calgon F-400[2]	1,050-1200	-	311	-	not available
IBC-109	761	781	277	284	2.5
Coal-Paint Mix	576	627	206	224	8.1
Paint Sludge	205	594	49.6	144	65.5
WBBP-B	707	895	134	170	21.0
SBBP-B	236	580	61.6	151	59.3
SBBP-A	767	783	223	228	< 2[3]
WBWP-B	64	323	7.1	35.9	80.2
SBWP-B	83	565	16.7	114	85.3
SBWP-A	124	756	24.6	150	83.6

[1] Data in this table are from a Calgon Technical Bulletin
[2] Data in this table are from Calgon Activated Carbon Product Bulletin
[3] The ash content of a sample of SBBP-A, not used in this study, was only 1.7%. Based on that determination, the value reported in the table is less than 2%.

Table 4: Freundlich Parameters for Chars and Calgon Carbons

Adsorbents	n	K, (mg/g) $(mg/L)^{-1/n}$ or Adsorption Capacity at 1 mg/L of p-Nitrophenol (mg/g)
Calgon BL	7.19	147
Calgon F-400	6.43	152
IBC-109	8.45	160
Coal-Paint Mix	8.65	121
Paint Sludge	7.51	26.9
WBBP-B	4.75	50.7
SBBP-B	5.59	27.0
SBBP-A	7.37	120
WBWP-B	4.32	2.44
SBWP-B	5.65	7.39
SBWP-A	20.5	19.7

3. The adsorption capacities of the black-paint chars were higher than those of the white-paint chars. The white-paint chars had a smaller surface area and higher ash content than the black-paint chars. The low adsorption capacity of the white-paint chars indicates that the pigment, titanium dioxide, did not appreciably participate in the adsorption of a compound such as p-nitrophenol. It remains to be seen whether this is also true for the adsorption of more hydrophilic compounds such as alcohols.

4. It is quite interesting to note that the paint-sludge char, which was produced from a paint sludge collected at an automotive assembly plant, where a variety of paints was used, showed an adsorption capacity which was between those of the black-paint chars and those of the white-paint chars. The ash content of the paint-sludge char was between those of the two groups of chars. This seems to support the initial idea that black paints would produce adsorbents with relatively high adsorption capacity among a variety of paints whereas white paints would do the opposite. The adsorption capacity of the paint-sludge char is approximately 18% (total weight based) and 48% (ash-free weight based) of that of Calgon BL. This adsorption capacity is still substantial, and the idea of putting a paint-sludge char back into a scrubber for capturing paint VOCs from the spray-booth air seems promising.

5. The coal-paint mix char showed a high adsorption capacity indicating that the addition of coal to improve the quality of the resulting char and to reduce ash content is feasible. As mentioned earlier, the char was produced from a mixture of coal and the solvent-borne white paint (manufacturer B). A material balance calculation based on the ash contents of the IBC-109, the coal-paint mix and the SBWP-B, indicate coal-paint mix char was produced from 7% SBWP-B and 93% IBC-109. The projected adsorption capacity of coal-paint mix, using the calculated composition and the individual adsorption capacities of SBWP-B and IBC-109, is 259 mg/g (total weight based), shown in Table 3. This is higher than the experimental value, 206 mg/g (total weight based). The difference may be the result of some blockage of pores by the titanium dioxide.

6. The slopes of all the paint-char isotherms (1 divided by the n in Table 4) are close to those of the Calgon carbons and are relatively flat (i.e., n is much greater than 1). This means that the adsorption capacity of a paint-sludge char can be efficiently used even at relatively low concentrations. In addition, the similar slopes indicate that the Calgon carbons and the paint chars have similar surface characteristics in terms of their affinity for p-nitrophenol because the slope roughly represents the adsorption energy.

7. The adsorption capacity at 100 mg/L of p-nitrophenol, which is listed in Table 3, is plotted against surface area in Figure 4. Both the amount adsorbed and the surface area in the top figure are based on total weight of the eleven adsorbents, whereas those in the bottom figure are based on ash-free weight of the same adsorbents. The solid lines are linear regression lines. The results show that the adsorption capacity appears to increase linearly with the surface area.

With regard to the possibility of implementing this pyrolysis process at an automobile assembly plant, one major factor is the amount of paint sludge available at the plant for

conversion to activated char and what fraction of the plant's activated carbon requirement could be met with its own sludge-derived adsorbent. The amount of sludge available may prove be too small to justify a dedicated facility for each assembly plant for making activated carbon. If so, it might be more economical to build a relatively large, centralized facility to which several assembly plants could send their paint sludges. This might be particularly true for the southeast region of Michigan where many assembly plants are located. In addition, blending the sludge with coal as feed at this centralized facility may not only improve the adsorption capacity of the resulting char but may be justified to meet the market demand of the area. Factor to consider in selecting a location of a central facility will include the amount of coal to be used, the transportation cost of coal from its source to the plant, and the shipping costs both for shipping paint sludge from the assembly plants to the central facility and for the return shipment of the product char to the assembly plants. Rough calculation at one plant indicate the quantity of adsorbent needed is several fold greater than would be produced from sludge. If that be generally true, it could prove economically attractive to ship all of the paint sludge to a coal producing area, and manufacture the adsorbent there. Disposition or regeneration of the spent adsorbent is another question to be answered.

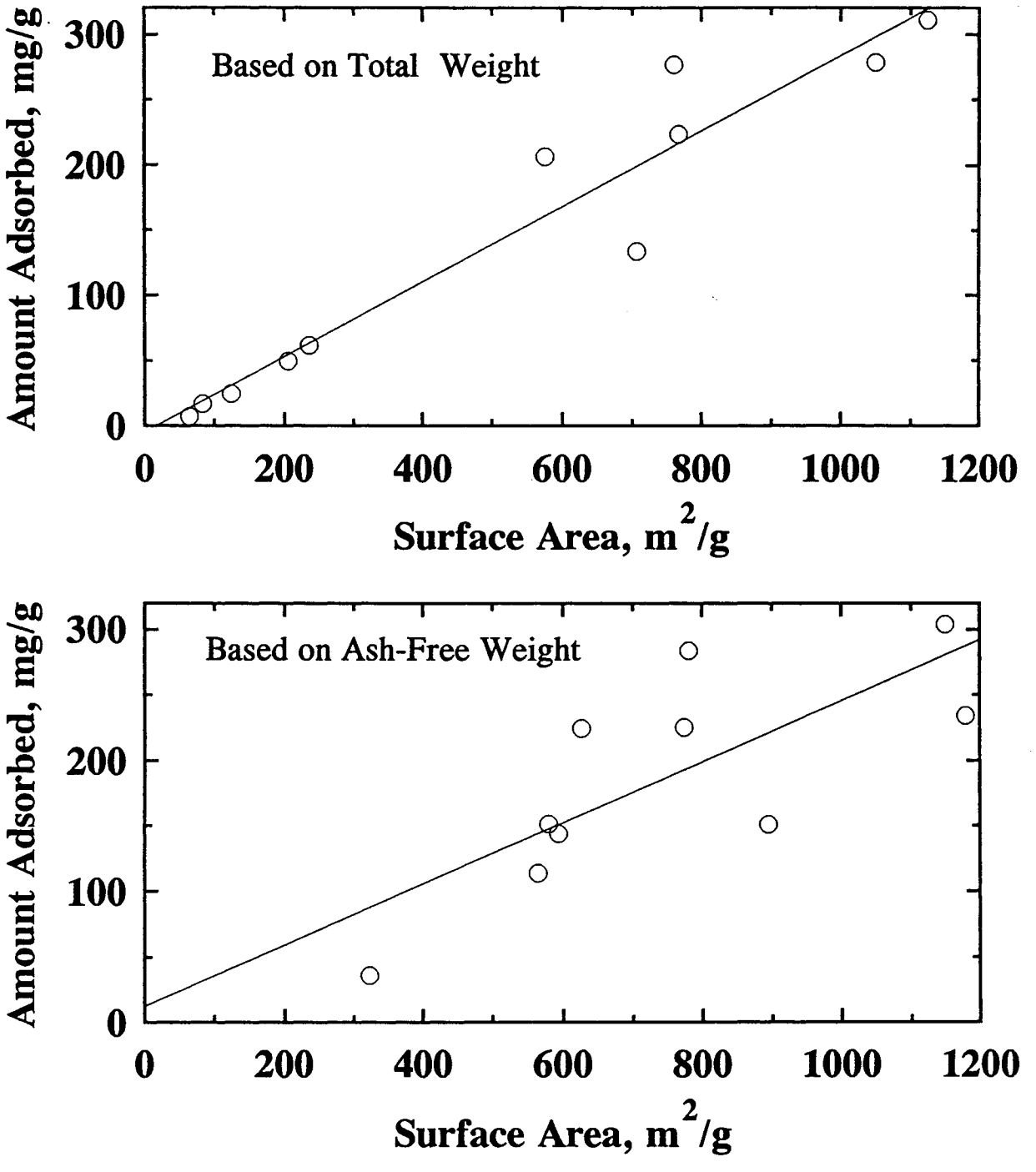

Figure 4: Effect of Surface Area of Char on the Adsorption Capacity for 100 mg/L of p-Nitrophenol

4.0 SUMMARY

The technical feasibility of producing activated carbon from real and simulated paint sludge was examined jointly by Ford Research Laboratory (FRL) and the Illinois State Geological Survey (ISGS). In this project, the ISGS produced nine chars using several dried paints, a paint sludge, a coal, and a coal-dried paint mixture. FRL conducted liquid-phase adsorption experiments using p-nitrophenol as an adsorbate to evaluate adsorption capacities of the chars and compared the results with those of commercially available activated carbons.

The primary findings are as follows:

- Unactivated paint chars had very little surface area and no appreciable capacity to adsorb p-nitrophenol. Activated carbons were produced from paint products by charring a 50:50 weight mixture of KOH and paint product and then carefully washing away the potassium hydroxide and other components solubilized by the strong base. Paint polymers being essentially the same, differences were not seen between solvent borne and water borne paints.

- The black-paint chars showed a substantially larger surface area than the white-paint chars, probably due to the white pigment, titanium dioxide, which is not expected to form a porous adsorbent material. Two black-paint chars, WBBP-B and SBBP-A, showed surface areas close to that of the IBC-109 char, an activated bituminous char produced under the same conditions as used for the black-paint chars.

- The black-paint chars, produced from manufacturer B's paints, showed unexpectedly high ash contents (21% for WBBP-B and 59.3% for SBBP-B) for a paint using carbon black as pigment.

- The ash content of the white-paint chars was very high (over 80%), as expected, because of the white pigment, titanium dioxide.

- The adsorption capacities of the Calgon carbons (BL and F-400) and IBC-109 carbon were comparable and were higher than those of the paint chars.

- The adsorption capacities of the black-paint chars were higher than those of the white-paint chars indicating that the pigment, titanium dioxide, did not participate appreciably in the adsorption of p-nitrophenol or in making the carbon structure more active.

- The paint-sludge char showed an adsorption capacity and an ash content between those of the black-paint chars and those of the white-paint chars, as expected from the fact that the sludge was formed from a variety of paints. The adsorption capacity of the paint-sludge char was found to be a little less than 20% (total weight based) and 50% (ash-free weight based) of the Calgon BL's.

- The fact that coal-paint mix char showed an adsorption capacity that was expected for the fraction of coal in the mix suggests that there is no synergism between the white

paint's titanium dioxide and coal for producing additional surface area or adsorption capacity. However, it was found that coal could be added to paint sludge to improve the quality of the resulting char and to reduce ash content.

- The slopes of the paint-char adsorption isotherms were close to those of the Calgon carbons and were relatively flat (i.e., n is much greater than 1), indicating that the adsorption capacity of a paint-sludge char could be efficiently used even at relatively low concentrations of p-nitrophenol.

- The adsorption capacity at 100 mg/L of p-nitrophenol was found to increase linearly with surface area.

- Chemical activation parameters were not optimized. A KOH/paint ratio other than 1/1 or the use of other chemical agents may improve the adsorption properties of chars derived from paint materials.

REFERENCES

Adamson, A.W. 1967. Physical Chemistry of Surfaces, 2nd edition. Interscience Publishers, a division of John Wiley & Sons, New York.

Berghoff, M. 1993. "DryPure Drying System to Process Waste Sludges." SAE Tech. Paper Ser. 930695, presented at 1993 SAE International Congress and Exposition, Detroit, MI.

Calgon Activated Carbon Product Bulletin 1068a. 1976.

Calgon Technical Bulletin Pulverized Activated Carbon. 23-1006.

Fritz, W. and Schlünder, E.U. 1981. "Competitive Adsorption of Two Dissolved Organics onto Activated Carbon - I. Adsorption Equilibria." Chem. Eng. Sci., 36, 721.

Weast, R.C. and Selby, S.M., eds. 1982. *Handbook of Chemistry and Physics*, 63rd edition, The Chemical Rubber Co., Cleveland, OH.

Jagtoyen, M., Thwaites, M., Stencel, J., Mcenaney, B., Derbyshire, F. 1992. "Adsorbent Carbon Synthesis from Coals by Phosphoric Acid Activation." Carbon, 30 (7), 1089-1096.

Kim, B.R. and Cognata, M.B. 1990. "PAC Addition as a Means of Regenerating GAC in a GAC Fluidized-Bed Reactor." Water Res., 24, 103.

Kim, B. R. and Pingel, L. J.. 1989. "Removal of Toluene from Air Using PAC/Water Slurry Reactor." J. Env. Eng., ASCE, 115, 1025.

Kim, B.R., Snoeyink, V.L., and Saunders, F.M. 1976. "Adsorption of Organic Compounds by Synthetic Resins." J. Water Pollut. Control Fed., 48, 120.

Kruse, C. W. and N. F. Shimp. 1981. "Removal of organic sulfur by low-temperature carbonization of Illinois coals." in Coal Processing Technology, Volume VII, "A Chemical Engineering Progress Technical Manual", AIChE, p. 124-134 (ISGS Reprint 1981E).

Kruse, C. W., N. F. Shimp, R. J. Helfinstine and J. D. Cooper. 1988. "Low-sulfur fuels from coals. U.S. Patent 4,758,331, July 19.

Snoeyink, V. L., Weber, W. J., Jr., and Mark, H. B. 1969. Sorption of Phenol and Nitrophenol by Active Carbon. Envir. Sci. & Tech., 3, 918.